CRYSTALLIZATION OF POTASSIUM MANGANATE

BY

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ARMOUR INSTITUTE OF TECHNOLOGY

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THE CRYSTALLIZATION OF POTASSIUM MANGANATE

A THESIS

PRESENTED BY

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TO THE

PRESIDENT AND FACULTY

OF

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OBJECT.

The object of this thesis is to determine the conditions under which potassium manganate crystallizes when crystallized from a solution containing (A) the excess of carbonate and hydroxide remaining in the fusion; (B) additional potassium hydroxide and (C) additional potassium carbonate. This involves chiefly the determination of the following conditions for each of the three cases:

1. Nature of the original solution with respect to
   - (a) Percentage of potassium manganate.
   - (b) Percentage of potassium hydroxide.
   - (c) Percentage of potassium carbonate.
   - (d) Specific gravity.
   - (e) Boiling point.
2. Nature of the solution at the time when crystals start to form on the surface with respect to
   - (a) Percentage of potassium manganate.
   - (b) Percentage of potassium hydroxide.
   - (c) Percentage of potassium carbonate.

(d) Specific gravity.

(e) Boiling point.

3. Nature of the crystals with respect to

(a) Percentage of potassium manganate.

(b) Percentage of potassium hydroxide.

(c) Percentage of potassium carbonate.

PREPARATION OF POTASSIUM MANGANATE

In order to understand the nature of the problem and the difficulties involved, it is well to consider first the methods of preparation and the properties of potassium manganate.

Potassium manganate, K_2MnO_4, is a very unstable salt, which may be prepared in many ways, which although similar vary greatly in detail.

According to Watt's "Dictionary of Chemistry", Vol. 3, 1892, p. 185, if a mixture of equal parts of finely powdered MnO_2 and KOH are heated to a bright red heat in air, or in oxygen, K_2MnO_4 is formed, according to the equation:

$$3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O$$

Potassium manganate is formed by heating MnO_2 and KOH, in the absence of oxygen, to 150°C. (Beketoff, Bulletin de la Société Chimique de Paris Vol. 1, p. 43); it is also formed in the presence of nitrogen at 180°C. (Elliot a. Storer, Proceedings of the American Academy of Arts and Sciences, Vol. 5, p. 192). Oxygen must be present if the mixture is heated above 180°C. because K_2MnO_4 is decomposed at 190°C., and MnO_2 is formed.

The equation given above represents the reaction which takes place when MnO_2 is fused with KOH in the absence of air (Roscoe and Schorlemmer, Treatise on Chemistry, Vol. 2, p. 1140 and Remsen, College Chemistry, p. 615).

Contrary to Watts, Mendeléeff in his "Principles of Chemistry" 3rd. ed. Vol. 2 (1905) p. 336 states that if MnO_2 or any lower oxide of manganese is heated with an alkali in the presence of air, the mixture absorbs oxygen and forms an alkaline manganate of green color, according to the equation:

$$2KOH + MnO_2 + O = K_2MnO_4 + H_2O$$

Steam is given off during the ignition and if this does not take place there is no absorption of oxygen.

The reaction is more rapid and a larger yield is obtained if $KClO_3$ or KNO_3 is added to the fusion.

$$3MnO_2 + 6KOH + KClO_3 = 3K_2MnO_4 + KCl + H_2O$$

(Remsen loc. cit.)

According to O. Sackur (Berichte, Vol. 43, p.381-8) when oxides of manganese are fused with an excess of K_2CO_3 or KOH the ratio of active oxygen to manganese quickly reaches, but does not exceed 1 : 1.6

although the amount of manganese oxidized increases with the time of the fusion. A compound of the formula $Mn_5O_{13}.5K_2O$ is formed in the fusion.

In another paper (Berichte Vol. 43, p. 448-53), O. Sackur found that results agreed with those of analysis only when the formula $K_2MnO_{3.6}$ was assigned to the dissolved salt; this formula might be written $3K_2MnO_4, 2K_2MnO_3$.

In a later paper (Berichte Vol. 44, p. 777-87), after a repetition of his previous work, he concludes that the compound $Mn_5O_{13}.8K_2O$ is the final product of the oxidation by the air of oxides of manganese dissolved in KOH or K_2CO_3, and that $Mn_5O_{13}.5K_2O$ is probably formed as an intermediate product.

Sackur claims (Zeitschrift Elektrochemie, Vol. 16, p. 649-54) after cryoscopic measurements with a complex mangani-manganate $2K_2MnO_3.3K_2MnO_4$ using fused K_2CO_3 as a solvent, that it is probable that a dissociation takes place:

$$2K_2MnO_3.3K_2MnO_4 = 2K_2MnO_3 + 3K_2MnO_4$$

and that it is impossible by any method to prepare pure K_2MnO_3 or K_2MnO_4 or any mixture of the two except in the ratio 2 : 3. By dissolving a mixture of the salts obtained by fusing MnO_2 with an

equivalent amount of KOH. in fused K_2CO_3, a partial decomposition takes place accompanied by the separation of a manganese compound, probably Mn_2O_3, until the proportion 2 : 3 has been reached.

The reaction between manganese dioxide, potassium hydroxide, and oxygen was studied by H. I. Schlesinger, R. D. Mullinix and S. Popoff (Journal of Industrial and Engineering Chemistry 1919 p. 317-23). They used a temperature of 450°C. in their fusions and their principal conclusions are (1) The yield of K_2MnO_4 varies greatly with the proportion of KOH used. At the temperatures used practically all of the MnO_2.is converted into manganate when 2.5 moles of KOH are used for each mole of MnO_2. (2) The reaction frequently stops before the maximum oxidation is reached. (3) The conclusion of Sackur that mangani-manganates are formed with a consequent yield of 60%, is thus proved incorrect. (4) Larger amounts of alkali cause a decomposition of manganate into a mangani-manganate similar to or identical with the one mentioned by Sackur.

The manganate fusion was further studied by P. Askenasy and S. Klonowski (Zeitschrift

Elektrochemie Vol. 16, p. 104-14). They studied the reaction

$MnO_2 + 2KOH + {}^1/_2O_2 = K_2MnO_4 + H_2O$

and found that the yield was increased by using an atmosphere of oxygen instead of air, and by maintaining a current of oxygen to remove the water formed in the reaction; powdered materials should be used. The reaction is fairly rapid at 250°C. but a temperature of 550°C. is recommended (yield 50-60%). At about 600°C. in air and about 700°C. in oxygen the yield is much smaller because the K_2MnO decomposes corresponding to the reversible reaction:

$K_2MnO_4 = K_2MnO_3 + {}^1/_2O_2$

MnO_2 cannot be heated above about 500°C. in oxygen, or 460°C. in air, without the decomposition into Mn_2O_3 and oxygen:

$2MnO_2 = Mn_2O_3 + 1/2O_2$

The reaction $Mn_2O_3 + 4KOH + 1{}^1/_2O_2 = 2K_2MnO_4 + 2H_2O$ is however similar to the MnO_2 reaction. There is some indication that K_2MnO_3 dissolves some K_2MnO_4 to form a solid solution.

The fusion methods for preparing potassium manganate are probably the best and are probably the ones most widely used. Another important

method for the preparation of potassium manganate is by boiling $KMnO_4$ Aq. with KOH Aq.

$$2KMnO_4 \text{ Aq.} + 2KOH \text{ Aq.} = 2K_2MnO_4 \text{ Aq.} + H_2O$$

(Aschoff, Journal fur praktische Chemie, Vol. 81, p. 29). According to Thenard (Journal fur praktische Chemie, Vol. 69, p. 58) this reaction only occurs when the KOH contains some oxidisable substance, such as a little organic matter; or according to Roscoe and Schorlemmer (Treatise on Chemistry, Vol. 2, p. 1139) when small amounts of reducing agents such as alcohol and sodium thiosulphate are added to the red alkaline liquid. Remsen (College Chemistry p. 615) claims that such substances aid the reaction, but if they are present the reduction goes further forming finally a manganite which is a derivative of the hydroxide $MnO(OH)_2$. By long continued heating of $KMnO_4$ to 240°C., K_2MnO_4 is formed according to the equation:

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

(Thenard , Journal fur praktische Chemie , Vol. 69, p. 58).

PROPERTIES AND REACTIONS.

When the manganate from the fusion is treated with a small amount of water, a dark green solution is formed which on evaporation in vacuum yields small, nearly black, crystals which are isomorphous with those of potassium sulphate and potassium chromate, namely six-sided prisms and pyramids. These crystals have the formula $K_2MnO_4 : MnO_3 \cdot K_2O$. On leaving a strong solution of potassium manganate exposed to the air, crystals of dimanganate, $2MnO_3 \cdot K_2O \cdot H_2O$, may be formed, the carbon dioxide of the air having withdrawn half the potash (System of Inorganic Chemistry, Ramsay 1891 p. 265).

According to Mendeleeff (Principles of Chemistry 3rd Ed. Vol. 2, 1905 p. 336) the composition of the product is not changed by being redissolved if perfectly pure water free from air and carbonic acid is taken. On the other hand Ramsay (System of Inorganic Chemistry 1891 p. 265) states that potassium manganate is stable only in the presence of an excess of alkali, and is decomposed by pure water with the formation of permanganate and manganese dioxide.

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + 4KOH + MnO_2$$

Remsen (College Chemistry p. 615) Watts (Dictionary of Chemistry Vol. 3 1892 p. 185) and Roscoe and Schorlemmer (Treatise on Chemistry Vol. 2 p. 1139)

agree with the latter, although it may be possible that the water they used was not as pure as that used by Mendeleéff.

In the presence of even very feeble acids the salt changes its color from green to red, and MnO_2 is deposited. The same decomposition takes place when the salt is heated with water, but when diluted with a large quantity of unboiled water MnO_2 does not separate, although the solution turns red; the change in color is caused by the change from K_2MnO_4 to $KMnO_4$. The reaction proceeding under the influence of acids and a large quantity of water, is expressed by the following equation

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH$$

When water containing atmospheric oxygen in solution acts on a solution of K_2MnO_4 the oxygen combines directly with the manganate and forms $KMnO_4$ without the precipitation of MnO_2.

$$2K_2MnO_4 + O + H_2O = 2KMnO_4 + 2KOH$$

This reaction is not reversible. Because of this characteristic change in color the salt is called mineral chameleon. The true explanation of the change of color is due to the researches of Chevillot, Edwards, Mitscherlich and Forchhammer who claim that the change of color of K_2MnO_4 is due to

its instability and to its splitting up into two other manganese compounds a higher and a lower

$$3MnO_3 = Mn_2O_7 + MnO_2$$

Manganese trioxide is decomposed in this manner by the action of water:

$$3MnO_3 + H_2O = 2MnHO_4 + MnO_2$$

(Franke, Thorpe, and Humbly).

The salt is very unstable and is deoxidized by organic matter with the formation of MnO_2 and alkali; therefore a solution of this salt cannot be filtered through filter paper or other organic material. The presence of a large quantity of free alkali increases the stability.

When the salt is heated, it breaks up in the presence of water, with the evolution of oxygen.

According to Watts (Dictionary of Chemistry, Vol. 3, 1892 p. 185) dilute acids, even CO_2 , quickly decompose K_2MnO_4 to form potassium permanganate and a manganous salt; for instance with H_2SO_4

$$5K_2MnO_4 + 4H_2SO_4 = 2K_2Mn_2O_8 + MnSO_4 + 3K_2SO_4 + 4H_2O$$

Molinari (General and Industrial Chemistry, Organic p. 625) gives the following reaction for H_2SO_4, the strength of the acid not being given:

$3K_2MnO_4 + 2H_2SO_4 = 2KMnO_4 + 2K_2SO_4 + MnO_2 + 2H_2O$

Remsen (College Chemistry p. 615) similarly claims that when a solution of manganate is treated with an acid, the manganic acid is at once decomposed into permanganic acid and manganese dioxide:

$3H_2MnO_4 = MnO_2 + 2H_2O + 2HMnO_4$

It has been my experience that the last reaction probably more nearly corresponds to the facts, as MnO_2 is formed.

According to Mendeleéff (Principles of Chemistry 3rd. ed. Vol. 2, 1905, p. 336) if a large proportion of acid is present and the decomposition is aided by heat the MnO_2 and $KMnO_4$ are also decomposed with the formation of a manganous salt. The decomposition that takes place under the action of acids also occurs in the presence of magnesium sulphate which reacts in many cases like an acid.

When carbon dioxide is passed into a solution of manganate a permanganate is formed:

$3K_2MnO_4 + 2CO_2 = 2K_2CO_3 + MnO_2 + 2KMnO_4$

Permanganate is also formed by boiling, or by allowing the solution of manganate to stand in the air.

Chlorine or ozone convert manganate into permanganate:

$K_2MnO_4 + Cl = KMnO_4 + KCl$

When K_2MnO_4 is heated in the presence of CS_2; MnS, CO_2 and polysulphides of potassium are formed (Muller, Poggendorff's Annalen der Physic und Chemie, Vol. 127, p. 404).

When heated in a stream of water vapor Mn_2O_3, KOH and O are produced.

$2K_2MnO_4 + 2H_2O = Mn_2O_3 + 4KOH + 3\ O$

By fusing MnO_2 and KOH together in the presence of air and then passing water vapor over the product, and then again fusing the products together and repeating the processes, oxygen may be obtained from the atmosphere.

O. Sackur and W. Taegener (Zeitschrift Elektrochemie Vol. 18, p. 718-24) working with aqueous solutions of potassium permanganate and potassium manganate secured the following results:

In strongly alkaline solutions the reaction

$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + 0.5\ O_2$

takes place on heating, while in weakly alkaline solutions the following reaction takes place:

$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH$

They could not use analytical methods, therefore they studied the reactions by determining equilibrium constants by measuring the potentials of (a) mixed solutions of $KMnO_4$ and K_2MnO_4 and (b) solutions of $KMnO_4$ using platinum electrodes against the normal electrode Hg/HgO in 0.8 N. KOH. In alkaline solutions the second reaction will go from left to right, in neutral or acid solutions from right to left.

Solubility of K_2MnO_4 in Aqueous Solutions
in Moles per Liter.

(Zeitschrift fur Elektrochemie Vol. 18, (1912), p. 724.

TEMPERATURE CENTIGRADE	2 N KOH	4 N KOH	6 N KOH	8 N KOH	10 N KOH
0	0.907	0.554	0.155	0.063	0.0145
10	1.013			0.070	0.0152
15			0.224		
17		0.681			
20	1.0140			0.078	0.0160
23			0.261		
25		0.733			
30	1.252	0.772	0.303	0.096	0.0215
40		0.852	0.362	0.119	0.0305
45	1.424	0.889	0.388		
50		* 0.938		0.142	0.0462
60		1.003	0.469	0.167	# 0.062
70		1.074	0.528	0.196	0.070
80		1.143	0.587	0.222	0.083

* 51°C.

63°C.

SOURCE OF MATERIAL AND PREPARATION OF POTASSIUM MANGANATE SOLUTIONS.

The potassium manganate used in this work was supplied by the Chemical Department of the Armour Institute of Technology; it was prepared by fusing potassium hydroxide and manganese dioxide in a muffle furnace. Water was added to the product of the fusion and the resulting dark green solution was filtered through an asbestos cloth on a Buchner funnel, in order to remove the manganese dioxide. Asbestos cloth was used because potassium manganate would rapidly attack paper, cloth, or other organic filtering medium.

The filtrate which amounted to about 5 liters was divided into three nearly equal portions:

(A) This portion contained chiefly potassium manganate, the excess of potassium hydroxide from the fusion, and potassium carbonate formed by the exposure of the hydroxide to the air or present in the original hydroxide.

(B) In addition to the materials listed in (A) a large amount of potassium hydroxide

was added.

(C) In addition to the materials listed in (A) a large amount of potassium carbonate was added.

The three solutions were kept in stoppered bottles and were ready for analysis.

METHODS FOR THE DETERMINATION OF POTASSIUM MANGANATE.

After considering the chemistry of potassium manganate there are several methods which suggest themselves as being of use in the quantitative determination of this compound; but I have found after much experimentation that most of them are worthless.

To be suitable for my needs the method had to be both rapid and fairly accurate. The first method which suggested itself was based on the following equation:

$$5K_2MnO_4 + 4H_2SO_4 = 2K_2Mn_2O_8 + MnSO_4 + 3K_2SO_4 + 4H_2O$$

The method was essentially as follows:

Weigh out a few grams of potassium manganate solution or about 1 gm. of the fusion, and take it up with about 50 cc of 5% KOH, because the manganate is stable in the presence of alkali, while pure water would decompose it. Filter the resulting green solution through an asbestos pad in a gooch crucible and wash with the dilute KOH until the washings are colorless. Transfer the washings to a 400 cc beaker by means of the dilute KOH and cautiously add dilute

H_2SO_4 (about 1-3) until the solution turns pink, and then add about 10 cc excess. Heat the solution to boiling, and titrate with an excess of N/10 oxalic acid and then back with N/10 $KMnO_4$ to the appearance of the first pink color.

This method seemed fairly promising and gave results which checked each other fairly well; but later I found the following equation for the reaction of sulphuric acid and potassium manganate:

$$3K_2MnO_4 + 2H_2SO_4 = 2KMnO_4 + 2K_2SO_4 + MnO_2 + 2H_2O$$

Upon further observation I noticed that MnO_2 was formed in the reaction but I was not certain that the reaction was taking place according to this equation, under the conditions of acid concentration, temperature etc., that I imposed upon it. This method was therefore abandoned.

A second method was based on the following equation:

$$K_2MnO_4 + Cl = KMnO_4 + KCl$$

This equation appears to offer a very simple method for the determination of potassium manganate, but in reality many difficulties are encountered.

The method as first tried, was essentially as follows:

The small sample of potassium manganate was transferred to a beaker by means of a stream of water, and the solution was diluted to about 100 cc. Chlorine gas was then bubbled through the solution until the color changed to red. The flow of chlorine was stopped and the solution was then boiled for several minutes to remove the excess of chlorine. It was cooled, 5 cc of H_2SO_4 added, heated to boiling, and the hot solution titrated with an excess of $N/10$ oxalic acid, and then the excess of oxalic acid titrated with $N/10$ $KMnO_4$. Check results were very difficult to obtain by this method.

After further experiment it occurred to me that I was introducing an error into the experiment by diluting the sample with water, because with water the reaction is probably as follows:

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + 4KOH + MnO_2$$

The first part of the method was therefore modified as follows:

A large sample of potassium manganate solution (about 10 gms.) was weighed into a

weighing bottle; this bottle was then placed within a 400 cc beaker and a stream of chlorine gas was passed into the liquid, while the liquid was gradually diluted with a dilute KOH solution. After the solution turned red, the flow of chlorine was stopped, and the solution boiled and titrated as before.

As I passed the chlorine into the solution I observed that the solution became warm; this suggested to me that potassium chlorate had been formed. According to Roscoe and Schorlemmer (Treatise on Chemistry Vol. 2, p. 333), when chlorine is passed into a concentrated solution of KOH or K_2CO_3, KOCl is formed as long as an excess of alkali is present

$$2KOH + Cl_2 = KOCl + KCl + H_2O$$

but as soon as the alkali is exhausted, and an excess of chlorine is present, the hypochlorite is suddenly converted into the chlorate with the evolution of much heat:

$$3KOCl = KClO_3 + 2KCl$$

A small deposit of MnO_2 was formed on the glass tube through which the chlorine was passed into the solution.

After boiling the solution for a short time the odor of chlorine could no longer be detected, but upon the addition of the dilute H_2SO_4.much chlorine was evolved, and MnO was precipitated, the liquid remaining only slightly pink. Oxalic acid cannot be used in the presence of chlorine.

This method could not be used because the reaction would not proceed according to the equation given.

Another method for the determination of K_2MnO_4 was outlined by P. Askenasy and S. Klonowski (Zeitschrift Elektrochemie, Vol. 16, p. 104-14) as follows. "The K_2MnO_4 was determined with $H_2C_2O_4$, after first adding water and filtering through an asbestos filter to remove the MnO_2". I did not try this method, but after considering the reactions of water, water containing CO_2, water containing oxygen, or water containing both CO_2 and oxygen as well as the effect of the dilution of the solution on potassium manganate, I am inclined to believe that this method would not give very satisfactory results.

METHOD USED.

The method used for the determination of potassium manganate was a modification of the Ford-Williams method (Lord and Demorest, Metallurgical Analysis p. 75). The method was as follows: To the sample of manganate 80 cc of concentrated HNO_3 free from nitrous fumes, sp. gr. 1.42, and 4gms. of $KClO_3$ were added, and the solution boiled gently for 10 minutes. 50 cc of concentrated HNO_3 and 4 gms. of $KClO_3$ were then added and the solution boiled for 10 minutes longer. The precipitate of MnO_2 was collected on an asbestos pad in a gooch crucible, washed three times with concentrated HNO_3 and three or more times with water. The precipitate was returned to the original beaker and dissolved in an excess of standard $FeSO_4$ solution. The solution was diluted to 150 cc and the excess of $FeSO_4$ titrated with standard $KMnO_4$ to the first permanent pink.

The method is based on the fact that when potassium chlorate is added to a solution of manganese in hot concentrated HNO_3, the manganese is all precipitated as MnO_2. The method measures total manganese and gives accurate results in a short time.

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

METHOD FOR THE DETERMINATION OF POTASSIUM HYDROXIDE AND POTASSIUM CARBONATE

Because of the nature of potassium manganate I was unable to devise a method for determining the exact amount of potassium carbonate and potassium hydroxide contained in my potassium manganate solutions. The method used, although probably the best available, was very unsatisfactory and the results obtained do not indicate the exact amounts of carbonate and hydroxide present, but probably give a crude approximation to the relative amounts contained in various solutions.

The method used for the determination of potassium hydroxide and potassium carbonate is based on the fact that with phenolphthalein as an indicator the number of cubic centimeters of standard acid used to make the solution neutral is a measure of all the KOH present plus one half of the K_2CO_3 present, and with methyl orange as an indicator, the titration measures all of the KOH plus all of the K_2CO_3, and the difference between the two titrations is a measure of one half of the K_2CO_3.

5-10 gms. of manganate solution were weighed into a weighing bottle. This bottle was opened and

placed in a 400 cc beaker and 10 cc of hot alcohol were poured over the sample. If the sample is solid the alcohol should be diluted before adding, because pure alcohol does not react. Heat the solution for a few minutes. This treatment changes the manganate to MnO_2 and it was at first thought that an amount of CO_2 equivalent to the K_2MnO_4 would be formed by the reaction of the manganate and alcohol, but later experiment proved that this was untrue; the chief product of the reaction was acetic acid, and a trace of acetaldehyde was also found. The solution was transferred to a 500 cc volumetric flask and diluted to the mark with 5% NaCl solution which had previously been neutralized with NaOH, using phenolphthalein as an indicator. The solution was filtered through a dry filter paper into a dry flask and aliquot portions of the filtrate were used for titration. The cold solution was first titrated with phenolphthalein as an indicator until the solution became colorless, then methyl orange was added and the titration continued to the pink end point.

Methyl Orange cc minus Phenolphthalein cc =
cc equivalent to 1/2 K_2CO_3.

Phenolphthalein cc minus cc equivalent to
1/2 K_2CO_3 = cc equivalent to KOH.

The titration is accurate only at 0°C. and in the presence of NaCl. This is one reason for the addition of the NaCl, and another is that it prevents the hydrolysis of the MnO_2.

By adding the alcohol before diluting the sample, the formation of additional KOH was prevented.

The presence of acetic acid was confirmed as follows: HCl was added to the filtrate obtained after filtering off the MnO_2, which treatment liberates the acetic acid, and the acetic acid was detected by adding ethyl alcohol and observing the odor of ethyl acetate. The odor was very strong, indicating a large amount of acetic acid.

The acetaldehyde was detected by observing the color produced with Schiff's reagent. The test showed only a trace of acetaldehyde.

Because of the formation of acetic acid and acetaldehyde it is impossible to correct the observed titrations so that the true amounts of carbonate and hydroxide present in the sample, are indicated.

Besides the difficulties mentioned, the method is also very unsatisfactory and difficult

to carry out because of the difficulty in recognising the end points.

METHODS FOR DETERMINING SPECIFIC GRAVITY.

The specific gravity of the original solutions was determined by means of a Westphal balance.

The specific gravity of the solutions at the time of crystallization was determined by pouring the hot solution into a tared 100 cc volumetric flask which after cooling was adjusted to the mark and weighed. The weight of this definite volume of liquid was then compared with the weight of the same volume of water, at the same temperature. This method was probably not very accurate but gave results which were accurate enough for our purpose. The presence of crystals prevented more accurate methods.

STANDARDISATION OF THERMOMETERS.

The thermometers used to measure the boiling points of the solutions were standardised by comparison with the readings of an accurate instrument.

PROCEDURE.

The solutions (A), (B), and (C) were first analysed for KOH, K_2CO_3 and K_2MnO_4 and the specific gravity taken.

600 gms. of each of these solutions were then placed in a large beaker and evaporated until a small crust of crystals formed on the surface of the boiling liquid. The boiling of the solutions both at the time the crystals formed, and at the start were observed. The previously standardised volumetric flasks were then filled with the hot liquid and after cooling, the specific gravities were determined. Samples to be used for KOH, K_2CO_3, and K_2MnO_4 were poured into tared weighing bottles and these constituents were later determined.

After allowing the evaporated solutions to stand for several days, the crystals were filtered on an asbestos cloth and allowed to drain. Because of their solubility they could not be washed. These crystals were dried almost completely in a dessicator and were finally dried for one half hour in a water oven. The dark green crystals were sampled and analysed for KOH, K_2CO_3, ahd K_2MnO_4.

STANDARDISATION OF THERMOMETERS USED.

STANDARD °C.	#1	CORR. #1	#2	CORR. #2	#3	CORR. #3
11.6	11.5	+ 0.1	11.6	0.0	11.9	- 0.3
14.6	14.4	+ 0.2	14.5	+ 0.1	14.9	- 0.3
20.7	20.6	+ 0.1	20.8	- 0.1	21.0	- 0.3
30.8	30.6	+ 0.2	31.0	- 0.2	31.0	- 0.2
40.8	40.9	- 0.1	41.0	- 0.2	41.0	- 0.2
50.7	50.9	- 0.2	51.0	- 0.3	51.0	- 0.3
59.7	59.7	0.0	59.6	+ 0.1	59.6	+ 0.1
69.7	69.8	- 0.1	69.8	- 0.1	69.8	- 0.1
80.6	80.6	0.0	80.8	- 0.2	80.7	- 0.1
90.5	90.5	0.0	90.6	- 0.1	90.5	0.0
101.6	101.6	0.0	102.0	- 0.4	101.8	- 0.2
202.2	102.2	0.0	102.2	0.0	102.7	- 0.5

STANDARDISATION OF PYCKNOMETERS.

100 cc glass stoppered volumetric flasks were used as pycknometers.

	No. 1.	No. 2.	No. 3.
Weight empty	33.5878	30.1402	33.2688
Plus H_2O @ 20°C.	133.5615	130.1260	133.3095
Weight of H_2O @ 20°	99.9737	99.9858	100.0407

STANDARD SOLUTIONS.

For "Original Solution" $FeSO_4$ and $KMnO_4$ of the following standard were used:

1 cc $KMnO_4$ $\equiv$ 0.73093 cc $FeSO_4$

1 cc $FeSO_4$ $\equiv$ 1.3681 cc $KMnO_4$

1 cc $FeSO_4$ $\equiv$ 0.014916 gm. $FeSO_4$ $\equiv$ 0.0096787 gm. K_2MnO_4

For all solutions except Run (A) (original) and all crystals HCl and NaOH of the following standard were used:

1 cc HCl $\equiv$ 0.63821 cc NaOH

1 cc NaOH $\equiv$ 1.56687 cc HCl

1 cc HCl $\equiv$ 0.0081839 gm KOH

1 cc HCl $\equiv$ 0.010079 gm K_2CO_3

For all solutions except the original, $FeSO_4$ and $KMnO_4$ of the following standard were used:

1 cc $KMnO_4$ $\equiv$ 1.0485 cc $FeSO_4$

1 cc $FeSO_4$ $\equiv$ 0.95375 cc $KMnO_4$

1 cc $KMnO_4$ $\equiv$ 0.0034610 gm $KMnO_4$

1 cc $FeSO_4$ $\equiv$ 0.015864 gm $FeSO_4$ $\equiv$ 0.010294 gm K_2MnO_4

For crystals and Run (A) (original) HCl of the following standard was used:

1 cc HCl $\equiv$ 0.0085234 gm KOH

1 cc HCl $\equiv$ 0.010497 gm K_2CO_3

RUN (A).

Solution to which no KOH or K_2CO_3 was added.

Original Solution.

Specific gravity = 1.1702 @ 15°C.

K_2MnO_4

A.	B.
1.5163 gm. sample	1.2636 gm. sample
used 5.20 cc $FeSO_4$ net	4.38 cc $FeSO_4$ net
3.32% K_2MnO_4	3.35% K_2MnO_4

Ave. 3.34% K_2MnO_4

KOH and K_2CO_3

A.	B.
3.3516 gm. sample	3.3701 gm. sample
used 38.95 cc HCl (Ph)	39.35 cc HCl (Ph)
and 46.60 cc (M.O.)	47.40 cc (M.O.)
KOH 7.96%	KOH 7.91%
K_2CO_3 4.79%	K_2CO_3 5.01%

Ave. KOH 7.94%

Ave. K_2CO_3 4.90%

RUN (A).

Evaporation.

Boiling point at start 102.3°C.

Boiling point at end 111.2°C. (Thermometer #1)

Specific gravity after evaporation 1.4034 @ 20°C.

K_2MnO_4

A.	B.
1.4621 gm. sample	1.4940 gm sample
used 8.04 cc $FeSO_4$ net	7.96 cc $FeSO_4$ net
5.66% K_2MnO_4	5.49% K_2MnO_4

Ave. 5.58% K_2MnO_4

KOH and K_2CO_3

A. 0.6809 gms.		B. 0.6122 gms.	
(1)	(2)	(1)	(2)
18.90 cc HCl (Ph)	18.55	15.85	15.70
22.09 cc HCl (M.O.)	21.50	18.12	17.95
KOH 18.88%	18.75%	18.15%	17.98%
K_2CO_3 9.44%	8.73%	7.47%	7.41%

Ave. KOH 18.44%

Ave. K_2CO_3 8.26%

RUN (A).

Crystals.

K_2MnO_4

A.	B.
0.5000 gm. sample	0.5000 gm. sample
used 40.48 cc $FeSO_4$ net	40.17 cc $FeSO_4$ net
83.34% K_2MnO_4	82.70% K_2MnO_4

Ave. 83.02% K_2MnO_4

KOH and K_2CO_3

	A.		B.	
	0.8000 gm. sample		0.8000 gm. sample	
	(1)	(2)	(1)	(2)
cc HCl (Ph)	17.29	17.22	18.20	18.12
cc HCl (M.O.)	24.80	24.80	24.80	24.80
KOH	10.42%	10.27%	12.36%	12.19%
K_2CO_3	19.71%	19.89%	17.32%	17.53%

Ave. KOH 11.31%

Ave. K_2CO_3 18.61%

RUN (B).

Solution to which 200 gms. additional KOH were added.

Original Solution.

Specific gravity 1.265 @ 15°C.

K_2MnO_4

A.	B.
2.7104 gm. sample	3.1489 gm. sample
used 8.92 cc $FeSO_4$ net	11.58 cc $FeSO_4$ net
3.19% K_2MnO_4	3.56% K_2MnO_4

Ave. 3.38% K_2MnO_4

KOH and K_2CO_3

	A.	B.
	1.2833 gm. sample	1.6405 gm. sample
	29.63 cc HCl (Ph)	38.37 cc HCl (Ph)
	35.60 cc HCl (M.O.)	45.88 cc HCl (M.O.)
KOH	15.09%	15.40%
K_2CO_3	9.38%	9.23%

Ave. KOH 15.25%

Ave. K_2CO_3 9.31%

RUN (B).

Evaporation.

Boiling point at start 107.5°C.

Boiling point at end 118°C. (Thermometer #2).

Specific gravity after evaporation 1.4217 @ 20°C.

K_2MnO_4

A.	B.
1.9740 gm. sample	1.4829 gm. sample
used 6.31 cc $FeSO_4$ net	4.08 cc $FeSO_4$ net
3.29% K_2MnO_4	3.10% K_2MnO_4

Ave. 3.20% K_2MnO_4

KOH and K_2CO_3

	A.		B.	
	0.6393 gm. sample		0.8028 gm. sample	
	(1)	(2)	(1)	(2)
cc HCl (Ph)	24.30	24.28	30.88	30.82
cc HCl (M.O.)	26.25	26.27	33.28	33.28
KOH	28.61%	28.53%	29.03%	28.91%
K_2CO_3	6.15%	6.26%	6.03%	6.18%

Ave. KOH 28.77%

Ave. K_2CO_3 6.16%

RUN (B).

Crystals.

K_2MnO_4

A.	B.
0.5000 gm. sample	0.5000 gm. sample
used 37.90 cc $FeSO_4$ net	37.90 cc $FeSO_4$ net
78.03% K_2MnO_4	78.03% K_2MnO_4

Ave. 78.03% K_2MnO_4

KOH and K_2CO_3

A.		B.
(1)	(2)	(1)
0.2000 gm. sample	0.4000 gm.	0.4000 gm.
used 4.80 cc HCl (Ph)	9.60	9.95
and 7.44 cc HCl (M.O.)	14.82	15.48
KOH 9.20%	9.33%	9.42%
K_2CO_3 27.71%	27.39%	29.02%

Ave. KOH 9.32%

Ave. K_2CO_3 28.04%

RUN (C).

Solution to which 200 gms. additional K_2CO_3 were added.

Original Solution.

Specific gravity 1.283 @ 15°C.

K_2MnO_4

A.	B.
1.4232 gm. sample	1.6077 gm. sample
used 3.39 cc $FeSO_4$ net	3.84 cc $FeSO_4$ net
2.30% K_2MnO_4	2.31% K_2MnO_4

Ave. 2.31% K_2MnO_4

KOH and K_2CO_3

	A.	B.
	2.0793 gm. sample	2.3920 gm. sample
used	32.58 cc HCl (Ph)	37.40
and	56.00 cc HCl (M.O.)	64.30
KOH	3.61%	3.59%
K_2CO_3	22.70%	22.67%

Ave. KOH 3.60%

Ave. K_2CO_3 22.69%

RUN (C).

Evaporation.

Boiling point at start 106.5°C.

Boiling point at end 117.5°C. (Thermometer #3).

Specific gravity after evaporation 1.5222 @ 20°C.

K_2MnO_4

A.	B.
1.1062 gm. sample	1.2270 gm. sample
used 3.84 cc $FeSO_4$ net	4.22 cc $FeSO_4$ net
3.57% K_2MnO_4	3.54% K_2MnO_4

Ave. 3.56% K_2MnO_4

KOH and K_2CO_3

	A. 0.8024 gm.		B. 0.9210 gm.	
	(1)	(2)	(1)	(2)
cc HCl (Ph)	23.00	23.20	26.85	26.82
cc HCl (M.O.)	35.10	35.15	40.82	40.88
KOH	11.12%	11.47%	11.44%	11.34%
K_2CO_3	30.40%	30.02%	30.58%	30.77%

Ave. KOH 11.34%

Ave. K_2CO_3 30.44%

RUN (C).

Crystals.

K_2MnO_4

A.	B.
0.5000 gm. sample	0.5000 gm. sample
used 38.11 cc $FeSO_4$ net	38.08 cc $FeSO_4$ net
78.46% K_2MnO_4	78.40% K_2MnO_4

Ave. 78.43% K_2MnO_4

KOH and K_2CO_3

0.2000 gm. samples

	A.		B.	
	(1)	(2)	(1)	(2)
cc HCl (Ph)	4.19	4.02	3.97	3.88
cc HCl (M.O.)	6.62	5.95	6.20	5.91
KOH	7.50%	8.91%	7.42%	7.88%
K_2CO_3	25.50%	20.26%	23.41%	21.31%

Ave. KOH 7.93%

Ave. K_2CO_3 22.62%

COMMENTS ON THE ANALYTICAL WORK.

Because of the limited time at my disposal and because of other difficulties in the work, it was almost imposible to secure entirely satisfactory results.

In some cases it was necessary to allow determinations to stand for a week before they could be finished; this caused many repeat analyses. Another fault that could not be remedied was the fact that it was necessary to allow the manganate solutions to stand for more than a month before they were evaporated; this may have caused some change in the composition of the solution although the change was probably small.

Other difficulties encountered were in the recognition of the phenolphthalein and methyl orange end points. It was observed that when the K_2CO_3 was present in small amounts while the percentage of KOH was large, that the end points were fairly distinct, but that if the percentage of K_2CO_3 was large the end points, especially the phenolphthalein end point, were very indistinct. It appears to be the case, although I cannot say for certain, that the rate of titration affects the phenolphthalein end point. If the acid is added slowly, drop by drop,

it will require more acid, and the pink color will fade very gradually, while if the acid is added very rapidly, the pink color will usually fade rapidly and less acid will be used. I have observed this in other cases especially if the amount of carbonate is high.

CONCLUSION.

The following results have been obtained using potassium manganate solutions containing (A) the excess of carbonate and hydroxide remaining in the fusion; (B) additional potassium hydroxide, and (C) additional potassium carbonate. The results obtained for KOH and K_2CO_3 do not show the exact composition of the solutions with respect to these salts, but give only an approximation to the relative amounts present.

Original Solutions.

	A.	B.	C.
K_2MnO_4	3.34%	3.38%	2.31%
KOH	7.94%	15.25%	3.60%
K_2CO_3	4.90%	9.31%	22.69%
Sp. Gr. @ 15°C.	1.1702	1.265	1.283
B. P.	102.3°C.	107.5°C.	106.5°C.

At Time Crystals Formed.

	A.	B.	C.
K_2MnO_4	5.58%	3.20%	3.56%
KOH	18.44%	28.77%	11.34%
K_2CO_3	8.26%	6.16%	30.44%
Sp. Gr. @ 20°C.	1.4034	1.4217	1.5222
B. P.	111.2°C.	118.0°C.	117.5°C.

Crystals.

	A.	B.	C.
K_2MnO_4	83.02%	78.03%	78.43%
KOH	11.31%	9.32%	7.93%
K_2CO_3	18.61%	28.04%	22.62%

From the results it may be seen that the addition of about 10% of KOH to the manganate solution lowers the percentage of K_2MnO_4 at the point of crystallization by about 2%, and also lowers the percentage of K_2MnO_4 in the crystals by about 5%. Likewise, the addition of about 15% of K_2CO_3 lowers the percentage of K_2MnO_4 at the point of crystallization by about 2%, and also lowers the percentage of K_2MnO_4 in the crystals by about 5%. The crystals obtained were mainly K_2MnO_4 , with considerable K_2CO_3, and a small amount of KOH.

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